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Specification as originally filed, with Application for Patent Serial No: **2,409,436**,  
on October 17, 2002, by **BAYER INC.**, assignee of Frédéric Guérin, for "Polymer  
Composites Comprising Low Molecular Weight Nitrile Rubber".

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**Polymer Composites Comprising Low Molecular Weight Nitrile Rubber****Abstract**

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The present invention relates to polymer composites comprising at least one, optionally hydrogenated, nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 30 at least one filler and optionally at least one cross-linking agent, a process for preparing said polymer composite wherein at least one, optionally hydrogenated, nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 30, at least one filler and optionally at least one cross-linking agent are mixed and a process for the manufacture of a shaped article comprising the step of injection molding a polymer composite comprising at least one, optionally hydrogenated, nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 30, at least one filler and at least one cross-linking agent.

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## **Polymer Composites Comprising Low Molecular Weight Nitrile Rubber**

### Field of the Invention.

The present invention relates to polymer composites comprising at least one nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 30 at least one filler and optionally at least one cross-linking agent, a process for preparing said polymer composite wherein at least one nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 30, at least one filler and optionally at least one cross-linking agent are mixed and a process for the manufacture of a shaped article comprising the step of injection molding a polymer composite comprising at least one nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 30, at least one filler and at least one cross-linking agent.

### Background of the Invention

Hydrogenated nitrile rubber (HNBR), prepared by the selective hydrogenation of acrylonitrile-butadiene rubber (nitrile rubber; NBR, a copolymer comprising at least one conjugated diene, at least one unsaturated nitrile and optionally further comonomers), is a specialty rubber which has very good heat resistance, excellent ozone and chemical resistance, and excellent oil resistance. Coupled with the high level of mechanical properties of the rubber (in particular the high resistance to abrasion) it is not surprising that NBR and HNBR have found widespread use in the automotive (seals, hoses, bearing pads) oil (stators, well head seals, valve plates), electrical (cable sheathing), mechanical engineering (wheels, rollers) and shipbuilding (pipe seals, couplings) industries, amongst others.

Commercially available HNBR has a Mooney viscosity in the range of from 55 to 105, a molecular weight in the range of from 200,000 to 500,000 g/mol, a polydispersity greater than 3.0 and a residual double bond (RDB) content in the range of from 1 to 18% (by IR spectroscopy).

One limitation in processing HNBR is the relatively high Mooney Viscosity. In principle, HNBR having a lower molecular weight and lower

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Mooney viscosity would have better processability. Attempts have been made to reduce the molecular weight of the polymer by mastication (mechanical breakdown) and by chemical means (for example, using strong acid), but such methods have the disadvantages that they result in the introduction of functional groups (such as carboxylic acid and ester groups) into the polymer, and the altering of the microstructure of the polymer. This results in disadvantageous changes in the properties of the polymer. In addition, these types of approaches, by their very nature, produce polymers having a broad molecular weight distribution.

A hydrogenated nitrile rubber having a low Mooney (<55) and improved processability, but which has the same microstructure as those rubbers which are currently available, is difficult to manufacture using current technologies. The hydrogenation of NBR to produce HNBR results in an increase in the Mooney viscosity of the raw polymer. This Mooney Increase Ratio (MIR) is generally around 2, depending upon the polymer grade, hydrogenation level and nature of the feedstock. Furthermore, limitations associated with the production of NBR itself dictate the low viscosity range for the HNBR feedstock. Currently, one of the lowest Mooney viscosity products available is Therban® VP KA 8837 (available from Bayer), which has a Mooney viscosity of 55 (ML 1+4 @ 100°C) and a RDB of 18%.

Co-pending applications CA-2,351,961, CA-2,357,470, CA 2,350,280 and CA 2,357,465 disclose a low-Mooney NBR and HNBR and a method for producing said low-Mooney NBR and HNBR. While the disclosed NBR or HNBR being perfectly suitable for the present invention, said applications are silent about polymer composites comprising said low-Mooney NBR and/or HNBR and methods of producing shaped articles from said low-Mooney NBR and/or HNBR.

#### Summary of the Invention

In one of its aspects, the present invention relates to a polymer composite comprising at least one nitrile rubber polymer ("NBR") having a Mooney viscosity (ML 1+4 @ 100°C) below 30, at least one filler and optionally at least one cross-linking agent. It is preferred that the NBR is fully or partially

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hydrogenated ("HNBR"). In particular, the invention relates to polymer composites comprising at least one, optionally hydrogenated, nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 20, preferably below 10.

5 In another one of its aspects, the present invention relates to a process for the manufacture of a shaped article comprising the step of injection molding a polymer composite comprising at least one, optionally hydrogenated, nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 30, at least one filler and at least one cross-linking agent.

10 Yet another aspect of the invention a shaped article, such as a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal or footwear component prepared by injection molding and subsequent curing of a polymer composite comprising at least one, optionally hydrogenated, nitrile rubber polymer having a Mooney viscosity (ML 1+4 @  
15 100°C) below 30, at least one filler and optionally at least one cross-linking agent.

#### Description of the Invention

As used throughout this specification, the term "nitrile polymer" or NBR  
20 is intended to have a broad meaning and is meant to encompass a copolymer having repeating units derived from at least one conjugated diene, at least one  $\alpha,\beta$ -unsaturated nitrile and optionally further one or more copolymerizable monomers.

The conjugated diene may be any known conjugated diene, in particular  
25 a C<sub>4</sub>-C<sub>6</sub> conjugated diene. Preferred conjugated dienes are butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. Even more preferred C<sub>4</sub>-C<sub>6</sub> conjugated dienes are butadiene, isoprene and mixtures thereof. The most preferred C<sub>4</sub>-C<sub>6</sub> conjugated diene is butadiene.

The  $\alpha,\beta$ -unsaturated nitrile may be any known  $\alpha,\beta$ -unsaturated nitrile, in  
30 particular a C<sub>3</sub>-C<sub>5</sub>  $\alpha,\beta$ -unsaturated nitrile. Preferred C<sub>3</sub>-C<sub>5</sub>  $\alpha,\beta$ -unsaturated nitriles are acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof. The most preferred C<sub>3</sub>-C<sub>5</sub>  $\alpha,\beta$ -unsaturated nitril is acrylonitril .

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Preferably, the copolymer comprises in the range of from 40 to 85 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 15 to 60 weight percent of repeating units derived from one or more unsaturated nitriles. More preferably, the copolymer comprises in the range of from 60 to 75 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 25 to 40 weight percent of repeating units derived from one or more unsaturated nitriles. Most preferably, the copolymer comprises in the range of from 60 to 70 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 30 to 40 weight percent of repeating units derived from one or more unsaturated nitriles.

Optionally, the copolymer may further comprise repeating units derived from one or more copolymerizable monomers, such as unsaturated carboxylic acids. Non-limiting examples of suitable unsaturated carboxylic acids are fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof. Repeating units derived from one or more copolymerizable monomers will replace either the nitrile or the diene portion of the nitrile rubber and it will be apparent to the skilled in the art that the above mentioned figures will have to be adjusted to result in 100 weight percent. In case of the mentioned unsaturated carboxylic acids, the nitrile rubber preferably comprises repeating units derived from one or more unsaturated carboxylic acids in the range of from 1 to 10 weight percent of the rubber, with this amount displacing a corresponding amount of the conjugated diolefin.

Other preferred optionally further monomers are unsaturated mono- or di-carboxylic acids or derivatives thereof (e.g., esters, amides and the like) including mixtures thereof.

Hydrogenated in this invention is preferably understood by more than 50 % of the residual double bonds (RDB) present in the starting nitrile polymer/NBR being hydrogenated, preferably more than 90 % of the RDB are hydrogenated, more preferably more than 95 % of the RDB are hydrogenated and most preferably more than 99 % of the RDB are hydrogenated.

The Mooney viscosity of the rubber was determined using ASTM test D1646.

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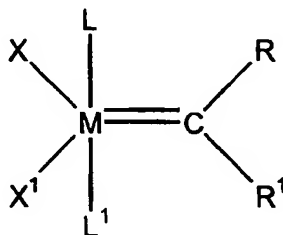
The inventive polymer composite comprises at least one, optionally hydrogenated, NBR having a Mooney viscosity (ML 1+4 @ 100°C according to ASTM test D1646) of less than 30, in particular less than 20, preferably less than 15 and even more preferably less than 10.

- 5 It is preferred that the low-Mooney, optionally hydrogenated NBR of this invention has a polydispersity index of less than 3, more preferred less than 2.9, even more preferred less than 2.8, even more preferred less than 2.7, even more preferred less than 2.6, even more preferred less than 2.5, even more preferred less than 2.4, even more preferred less than 2.3, and even  
10 more preferred less than 2.2.

The present invention is not restricted to a special process for preparing the optionally hydrogenated NBR. However, the NBR/HNBR of the invention is readily available in a two step synthesis as disclosed in CA-2,351,961, CA-2,357,470, CA 2,350,280 and CA 2,357,465, which may take place in the same  
15 reaction set-up or different reactors. For jurisdictions allowing for this procedure, CA-2,351,961, CA-2,357,470, CA 2,350,280 and CA 2,357,465 are incorporated herein by reference.

### Step 1: Metathesis

- 20 The metathesis reaction is conducted in the presence of one or more compounds of the general formulas I, II, III or IV;



Formula I

wherein:

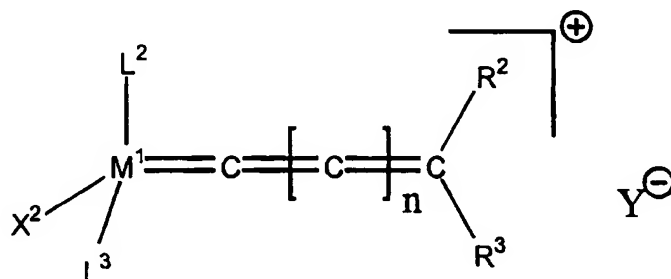
- 25 M is Os or Ru,  
R and R<sup>1</sup> are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub>

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carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfanyl,

X and X<sup>1</sup> are independently any anionic ligand, and

- 5 L and L<sup>1</sup> are independently any neutral ligand, such as phosphines, amines, thioethers or imidazolidinylidenes or any neutral carbene, optionally, L and L<sup>1</sup> can be linked to one another to form a bidentate neutral ligand;



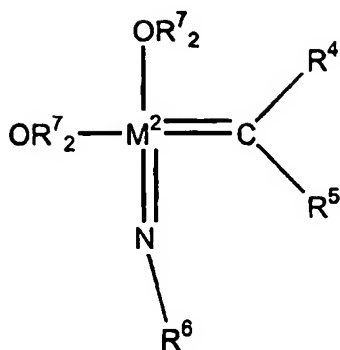
Formula II

wherein:

- 10 M<sup>1</sup> is Os or Ru;  
 R<sup>2</sup> and R<sup>3</sup> are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfanyl,  
 15 X<sup>2</sup> is a anionic ligand, and  
 L<sup>2</sup> is a neutral  $\pi$ -bonded ligand, independent of whether they are mono- or polycyclic,  
 L<sup>3</sup> is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines,  
 20 Y<sup>-</sup> is a non-coordinating anion,  
 n is an integer in the range of from 0 to 5;



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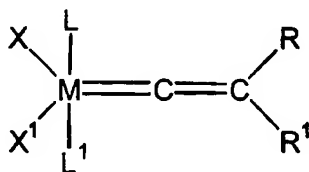
Formula III

wherein

 $\text{M}^2$  is Mo or W,

5  $\text{R}^4$  and  $\text{R}^5$  are, independently, hydrogen or a hydrocarbon selected from the group consisting of C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl and C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl,

10  $\text{R}^6$  and  $\text{R}^7$  are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof,



Formula VI

wherein:

M is Os or Ru,

15 R and  $\text{R}^1$  are independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, and substituted or unsubstituted alkyl,

 $\text{X}$  and  $\text{X}^1$  are independently any anionic ligand, and

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L and L<sup>1</sup> are independently any neutral ligand, such as phosphines, amines, thioethers or imidazolidinylidenes or any neutral carbene, optionally, L and L<sup>1</sup> can be linked to one another to form a bidentate neutral ligand;

Compounds of Formula I are preferred. Compounds of Formula I  
 5 wherein L and L<sup>1</sup> are trialkylphosphines, X and X<sup>1</sup> are chloride ions and M is Ruthenium are even more preferred.

The amount of compounds will depend upon the nature and catalytic activity of the compound(s) in question. Typically, the ratio of compound(s) to NBR is in the range of from 0.005 to 5, preferably in the range of from 0.025 to  
 10 1 and, more preferably, in the range of from 0.1 to 0.5.

The metathesis reaction is carried out in the presence of a co-olefin which is preferably a C<sub>2</sub> to C<sub>16</sub> linear or branched olefin such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is preferably in the range of from 1  
 15 to 200 weight %. Where the co-olefin is a gas (such as ethylene) the amount of co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from 1 \* 10<sup>5</sup> Pa to 1 \* 10<sup>7</sup> Pa, preferably in the range of from 5.2 \* 10<sup>5</sup> Pa to 4 \* 10<sup>6</sup> Pa.

The metathesis reaction can be carried out in any suitable solvent which  
 20 does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

25 The concentration of nitrile polymer (NBR) in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from 1 to 20% by weight, most preferably in the range of from 6 to 15% by weight.

30 The metathesis reaction is carried out at a temperature in the range of from 20 to 140°C; preferably in the range of from 60 to 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which

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the reaction is performed. The metathesis is usually complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity. Whenever referenced throughout the specification the

5 molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millenium software version 3.05.01. Samples were dissolved in tetrahydrofuran (THF) stabilized with 0.025% BHT. The columns used for the determination were three sequential

10 mixed-B gel columns from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

### **Step 2: Hydrogenation**

After the metathesis reaction, the nitrile polymer must be hydrogenated

15 to result in a partially or fully hydrogenated nitrile polymer (HNBR). HNBR are preferred in the present invention. Reduction of the product from the metathesis reaction can be effected using standard reduction techniques known in the art. For example, homogeneous hydrogenation catalysts known to those of skill in the art, such as Wilkinson's catalyst  $\{(PPh_3)_3RhCl\}$  and the

20 like can be used.

The hydrogenation may be performed *in situ* i.e. in the same reaction vessel in which the metathesis step is carried out, without the need to first isolate the metathesised product. The hydrogenation catalyst is simply added to the vessel, which is then treated with hydrogen to produce the HNBR.

25 Grubb's catalyst, in the presence of hydrogen, is converted to a dihydride complex  $(PR_3)_2RuCl_2H_2$ , which is itself an olefin hydrogenation catalyst. Thus, in a favorable one-pot reaction, Grubb's catalyst was used to reduce the molecular weight of NBR in the presence of co-olefin. The reaction mixture was then treated with hydrogen, converting the Grubb's complex to the

30 dihydride species which then hydrogenated the metathesis product to produce the HNBR of the invention. The rate of hydrogenation was lower in this case than in the case where Wilkinson's catalyst was used for the hydrogenation step, but it is clear that such an approach is indeed a viable one.

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The low Mooney NBR as well as the low Mooney HNBR which forms a preferred component of the polymer composite of the invention can be characterized by standard techniques known in the art. For example, the molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millennium software version 3.05.01. Samples were dissolved in tetrahydrofuran (THF) stabilized with 0.025% BHT. The columns used for the determination were three sequential mixed-B gel columns from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

The inventive polymer composite further comprises at least one filler. The filler may be an active or an inactive filler or a mixture thereof. The filler may be in particular:

- highly dispersed silicas, prepared e.g. by the precipitation of silicate solutions or the flame hydrolysis of silicon halides, with specific surface areas of in the range of from 5 to 1000 m<sup>2</sup>/g, and with primary particle sizes of in the range of from 10 to 400 nm; the silicas can optionally also be present as mixed oxides with other metal oxides such as those of Al, Mg, Ca, Ba, Zn, Zr and Ti;
- synthetic silicates, such as aluminum silicate and alkaline earth metal silicate like magnesium silicate or calcium silicate, with BET specific surface areas in the range of from 20 to 400 m<sup>2</sup>/g and primary particle diameters in the range of from 10 to 400 nm;
- natural silicates, such as kaolin and other naturally occurring silica;
- glass fibers and glass fiber products (matting, extrudates) or glass microspheres;
- metal oxides, such as zinc oxide, calcium oxide, magnesium oxide and aluminum oxide;
- metal carbonates, such as magnesium carbonate, calcium carbonate and zinc carbonate;
- metal hydroxides, e.g. aluminum hydroxide and magnesium hydroxide;

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- carbon blacks; the carbon blacks to be used here are prepared by the lamp black, furnace black or gas black process and have preferably BET (DIN 66 131) specific surface areas in the range of from 20 to 200 m<sup>2</sup>/g, e.g. SAF, ISAF, HAF, FEF or GPF carbon blacks;
- rubber gels, especially those based on polybutadiene, butadiene/styrene copolymers, butadiene/acrylonitrile copolymers and polychloroprene;

or mixtures thereof.

- 10 Examples of preferred mineral fillers include silica, silicates, clay such as bentonite, gypsum, alumina, titanium dioxide, talc, mixtures of these, and the like. These mineral particles have hydroxyl groups on their surface, rendering them hydrophilic and oleophobic. This exacerbates the difficulty of achieving good interaction between the filler particles and the rubber. For
- 15 many purposes, the preferred mineral is silica, especially silica made by carbon dioxide precipitation of sodium silicate. Dried amorphous silica particles suitable for use in accordance with the invention may have a mean agglomerate particle size in the range of from 1 to 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns.
- 20 It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover usually has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of in the range of from 50 and 450 square meters per gram and a DBP absorption, as measured in accordance
- 25 with DIN 53601, of in the range of from 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/11, of in the range of from 0 to 10 percent by weight. Suitable silica fillers are available under the trademarks HiSil® 210, HiSil® 233 and HiSil® 243 from PPG Industries Inc. Also suitable are Vulkasil® S and Vulkasil® N, from Bayer AG.
- 30 Often, use of carbon black as a filler is advantageous. Usually, carbon black is present in the polymer composite in an amount of in the range of from 20 to 200 parts by weight, preferably 30 to 150 parts by weight, more preferably 40 to 100 parts by weight. Further, it might be advantageous to use

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a combination of carbon black and mineral filler in the inventive polymer composite. In this combination the ratio of mineral fillers to carbon black is usually in the range of from 0.05 to 20, preferably 0.1 to 10.

The polymer composite may advantageously further comprise other  
 5 natural or synthetic rubbers such as BR (polybutadiene), ABR  
 (butadiene/acrylic acid- $C_1$ - $C_4$ -alkylester-copolymers), CR (polychloroprene), IR  
 (polyisoprene), SBR (styrene/butadiene-copolymers) with styrene contents in  
 the range of 1 to 60 wt%, NBR (butadiene/acrylonitrile-copolymers with  
 acrylonitrile contents of 5 to 60 wt%, HNBR with a Mooney viscosity (ML 1+4  
 10 @ 100°C according to ASTM test D1646) of at least 30 (partially or totally  
 hydrogenated NBR-rubber), EPDM (ethylene/propylene/diene-copolymers),  
 FKM (fluoropolymers or fluororubbers), and mixtures of the given polymers.  
 Careful blending with conventional HNBR often reduces cost of the polymer  
 composite without sacrificing the processability. The amount of conventional  
 15 HNBR and/or other natural or synthetic rubbers will depend on the process  
 condition to be applied during manufacture of shaped articles and is readily  
 available by few preliminary experiments.

The polymer composite furthermore optionally comprises one or more  
 cross-linking agents or curing systems. The invention is not limited to a special  
 20 curing system, however, peroxide curing system are preferred. Furthermore,  
 the invention is not limited to a special peroxide curing system. For example,  
 inorganic or organic peroxides are suitable. Preferred are organic peroxides  
 such as dialkylperoxides, ketalperoxides, aralkylperoxides, peroxide ethers,  
 peroxide esters, such as di-tert.-butylperoxide, bis-(tert.-butylperoxyisopropyl)-  
 25 benzene, dicumylperoxide, 2,5-dimethyl-2,5-di(tert.-butylperoxy)-hexane, 2,5-  
 dimethyl-2,5-di(tert.-butylperoxy)-hexene(3), 1,1-bis-(tert.-butylperoxy)-3,3,5-  
 trimethyl-cyclohexane, benzoylperoxide, tert.-butylcumylperoxide and tert.-  
 butylperbenzoate. Usually the amount of peroxide in the polymer composite is  
 in the range of from 1 to 10 phr (= per hundred rubber), preferably from 4 to 8  
 30 phr. Subsequent curing is usually performed at a temperature in the range of  
 from 100 to 200 °C, preferably 130 to 180 °C. Peroxides might be applied  
 advantageously in a polymer-bound form. Suitable systems are commercially

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available, such as Polydispersion T(VC) D-40 P from Rhein Chemie Rheinau GmbH, D (= polymerbound di-tert.-butylperoxy-isopropylbenzene).

The rubber composition according to the invention can contain further auxiliary products for rubbers, such as reaction accelerators, vulcanizing  
 5 accelerators, vulcanizing acceleration auxiliaries, antioxidants, foaming agents, anti-aging agents, heat stabilizers, light stabilizers, ozone stabilizers, processing aids, plasticizers, tackifiers, blowing agents, dyestuffs, pigments, waxes, extenders, organic acids, inhibitors, metal oxides, and activators such as triethanolamine, polyethylene glycol, hexanetriol, etc., which are known to  
 10 the rubber industry. The rubber aids are used in conventional amounts, which depend inter alia on the intended use. Conventional amounts are e.g. from 0.1 to 50 wt.%, based on rubber. Preferably the composition comprises in the range of 0.1 to 20 phr of an organic fatty acid as an auxiliary product, preferably a unsaturated fatty acid having one, two or more carbon double  
 15 bonds in the molecule which more preferably includes 10% by weight or more of a conjugated diene acid having at least one conjugated carbon-carbon double bond in its molecule. Preferably those fatty acids have in the range of from 8-22 carbon atoms, more preferably 12-18. Examples include stearic acid, palmitic acid and oleic acid and their calcium-, zinc-, magnesium-,  
 20 potassium- and ammonium salts. Preferably the composition comprises in the range of 5 to 50 phr of an acrylate as an auxiliary product. Suitable acrylates are known from EP-A1-0 319 320, in particular p. 3, l. 16 to 35, from US-5 208 294, in particular Col. 2, l. 25 to 40, and from US-4 983 678, in particular Col. 2, l. 45 to 62. Particular reference is made to zinc acrylate, zinc diacrylate  
 25 or zinc dimethacrylate or a liquid acrylate, such as trimethylolpropanetrimethacrylate (TRIM), butanedioldimethacrylate (BDMA) and ethylenglycoldimethacrylate (EDMA). It might be advantageous to use a combination of different acrylates and/or metal salts thereof. Of particular advantage is often to use metal acrylates in combination with a Scorch-retarder  
 30 such as sterically hindered phenols (e.g. methyl-substituted aminoalkylphenols, in particular 2,6-di-tert.-butyl-4-dimethylaminomethylphenol).

The ingredients of the final polymer composite are mixed together, suitably at an elevated temperature that may range from 25 °C to 200 °C.

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Normally the mixing time does not exceed one hour and a time in the range from 2 to 30 minutes is usually adequate. The mixing is suitably carried out in an internal mixer such as a Banbury mixer, or a Haake or Brabender miniature internal mixer. A two roll mill mixer also provides a good dispersion of the additives within the elastomer. An extruder also provides good mixing, and permits shorter mixing times. It is possible to carry out the mixing in two or more stages, and the mixing can be done in different apparatus, for example one stage in an internal mixer and one stage in an extruder. However, it should be taken care that no unwanted pre-crosslinking (= scorch) occurs during the mixing stage. For compounding and vulcanization see also: Encyclopedia of Polymer Science and Engineering, Vol. 4, p. 66 et seq. (Compounding) and Vol. 17, p. 666 et seq. (Vulcanization).

Due to the low viscosity of the polymer composite, the polymer composite is ideally suited to be processed by but not limited to molding injection technology. The polymer composite can also be useful to transfer molding, to compression molding, to liquid injection molding. The polymer composite comprising a cross-linking system is usually introduced in a conventional injection molding and injected into hot (about 160-230°C) forms where the cross-linking/vulcanization takes place depending on the polymer composite composition and temperature of the mold.

The inventive polymer composite is very well suited for the manufacture of a shaped article, such as a seal, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, pipe seal, in place gaskets or footwear component prepared by injection molding technology.



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**EXAMPLES****Example 1**

5 Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene and monochlorobenzene (MCB) were purchased from Alfa, Aldrich Chemicals, and PPG respectively and used as received. Perbunan was obtained from Bayer Inc.

The **metathesis** reactions were carried out in a pilot size reactor under the following conditions:

10	Cement Concentration	6%
	Co-Olefin	Ethylene
	Co-Olefin Concentration	500 psi
	Agitator Speed	600 rpm
	Reactor Temperature	80°C
15	Catalyst Loading	0.25 phr
	Solvent	Monochlorobenzene
	Substrate	statistical Butadiene-acrylonitrilecopolymer with a acrylonitrile content of 34 mol% and a
20		Mooney-Viscosity ML (1+4)@ 100 deg. C of 35

The polymer (9 kg) was dissolved in monochlorobenzene (141 kg). The reactor was heated to desired temperature and 2 L of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor. The reactor was pressurized with ethylene to a pressure of 500psi. The temperature was maintained constant for the duration of the reaction. A cooling coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements.

30 The **hydrogenation** reactions were carried out in the same reactor as the metathesis under the following conditions:

Cement solid concentration	6%
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	H <sub>2</sub> (g) pressur	1200 psi
	Agitator Speed	600 rpm
	Reactor Temperature	138°C
	Catalyst Loading (Wilkinson's)	0.075 phr
5	Triphenylphosphine	1 phr
	Solvent	Monochlorobenzene

The cement from the metathesis reaction was degassed 3 times with H<sub>2</sub> (100 psi) under full agitation. The temperature of the reactor was raised to 130°C and a 1L monochlorobenzene solution containing Wilkinson's catalyst and triphenylphosphine was added to the reactor. The temperature was allowed to increase to 138°C and maintained constant for the duration of the reaction. The hydrogenation reaction was monitored by measuring the residual double bond (RDB) level at various intervals using IR spectroscopy.

Alternatively, the Ruthenium metathesis catalyst could be used to hydrogenate the polymer.

#### Examples 2-6: Compounding and physical testing

Polymer composites were mixed on an open mill. The curatives were added on a cold open mill in a separate mixing step. The formulations used in this assessment are based on a simplified peroxide recipe according to Table 1.

Carbon black N 660 Sterling-V available from Cabot Tire Blacks

Maglite® D is a MgO available from C.P. Hall.

Naugard® 445 is a diphenylamine available from Uniroyal Chemical.

Plasthall TOTM is a Trioctyl trimellitate available from C.P. Hall.

Vulkanox® ZMB-2/C5 is a Zinc salt of 4- and 5-methyl-mercapto benzimidazole available from Bayer AG

DIAC #7 is a Triallylisocyanurate available from DuPont Dow Elastomers

Vulcup 40KE is 2,2'-bis (tert-butylperoxy di-isopropylbenzene) available from Harwick Standard.

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**Table 1 Compounding Recipe**

Experiment	2	3	4	5	6
	(comp.)				(comp.)
Therban® A3407	100				100
HNBR of Example 1		100	100	100	
Carbon Black, N 660 Sterling-V	50	50	50	50	50
Maglite® D	3	3	3	3	3
Naugard® 445	1	1	1	1	1
Plasthall TOTM	5				
Vulkanox® ZMB-2/C5 (ZMMBI)	0.4	0.4	0.4	0.4	0.4
Zinc Oxide (Kadox® 920) Grade PC 216	3	3	3	3	3
<b>Curatives</b>					
DIAC #7	1.5	2	2.4	2.8	1.5
Vulcup 40KE	7.5	10	12	14	7.5

Polymer Properties

- A summary of the raw polymer properties is shown in Table 2. The molecular weight (Mw) of the Polymer of Example 1 is ¼ that of regular Therban® A3407 while the narrow polydispersity (PDI) is 2.1 compared to 3.2 for the regular grade.

**Table 2 Summary of Raw Polymer Properties**

	Mn	Mw	PDI	ML 1+4 @ 100 °C
Polymer from Exp. 1	37000	76000	2.1	6.5
Therban® A3407	97000	314000	3.2	70.5

10 Polymer Composites Properties

Table 3 shows a summary of the properties of polymer composites of Exp. 2-6. Examples 2 and 6 are for comparison.

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**Table 3 Summary of Polymer Composites Properties**

<b>Example</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>Mooney ML 1+4@100°C</b>					
<b>- Raw Polymer</b>	70	← 6.5 →			70
<b>- Polymer composite</b>	91.0	16.8	16.0	15.4	107.8
<b>MH (dN.m)</b>	51.4	37.5	50.5	62.6	58.7
<b>ML (dN.m)</b>	3.1	0.1	0.1	0.1	3.8
<b>Delta Torque (dN.m)</b>	48.3	37.4	50.4	62.5	54.6
<b>t90 (minutes)</b>	13.7	16.7	15.8	14.6	13.7
<b>100% Modulus (Mpa)</b>	7.8	9.3	13.3	17.9	9.2
<b>Ultimate Tensile (Mpa)</b>	23.3	19.5	19.3	18.4	25.6
<b>Elongation at Break (%)</b>	211	172	132	102	202
<b>Hardness Shore A</b>	68	69	71	73	70
<b>Compression Set in % after 168h @ 150°C</b>	20.14	22.85	21.69	20.67	22.54
<b>DIN Abrasion</b>	86	125	126	124	76
<b>Heat Rise (°C)</b>	28	32	27	24	29
<b>Permanent Set (%)</b>	0.7	0.4	0.3	0.2	0.4

From Table 3, it is clear that although the molecular weight (Mw) of the Low Mooney HNBR used in polymer composites 2-5 is only ¼ that of Therban® A3407, the physical properties remain very good. The excellent physical properties of such a low molecular weight polymer might be attributed to the narrow molecular weight distribution. The low molecular weight and the narrow MWD result in a favorable viscosity which allows for injection molding processes for producing shaped articles.

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**Claims**

1. A polymer composite comprising at least one, optionally hydrogenated,  
nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C)  
5 below 30, at least one filler and optionally at least one cross-linking  
agent.
2. A polymer composite according to claim 1 wherein the raw polymer  
Mooney viscosity (ML 1+4 @ 100°C) is below 20.  
10
3. A polymer composite according to claim 1 wherein the raw polymer  
Mooney viscosity (ML 1+4 @ 100°C) is below 10.
4. A polymer composite according to any of claims 1-3 wherein the  
15 polymer composite comprises a peroxide, resin or sulfur curing system.
5. A process for preparing a polymer composite according to any of claims  
1-4 wherein at least one, optionally hydrogenated, nitrile rubber polymer  
having a Mooney viscosity (ML 1+4 @ 100°C) below 30, at least one  
20 filler and optionally at least one cross-linking agent are mixed.
6. A process for the manufacture of a shaped article comprising the step of  
injection molding a polymer composite comprising at least one,  
optionally hydrogenated, nitrile rubber polymer having a Mooney  
25 viscosity (ML 1+4 @ 100°C) below 30, at least one filler and at least one  
cross-linking agent.
7. A process according to claim 6, wherein the shaped article is seal,  
gasket, belt, hose, bearing pad, stator, well head seal, valve plate, cable  
30 sheathing, wheel, roller, in place gaskets or pipe seal.

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8. A process for the manufacture of a shaped article comprising the step of liquid injection molding a polymer composite comprising at least one, optionally hydrogenated, nitrile rubber polymer having a Mooney viscosity (ML 1+4 @ 100°C) below 10, at least one filler and at least one cross-linking agent.
9. A process according to claim 8, wherein the shaped article is seal, gasket, belt, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel, roller, in place gaskets or pipe seal.